PHY 742 Quantum Mechanics II
1-1:50 AM MWF via video link:
https://wakeforest-university.zoom.us/my/natalie.holzwarth

Extra notes for Lecture 29

Hartree-Fock approximation; specifically applied to the analysis of a multi electron atom

This material is not explicitly treated in your textbook, but does build on what we learned in Chapter 10.

1. **Review and motivation**
2. **The Hartree-Fock analysis**
3. **Hartree-Fock analysis specifically for an atom**

This topic is not explicitly covered in your textbook. There are quite a few sources on the internet and I will try to suggest a few as well. The Hartree-Fock method is a venerable method for reasonably accurate modeling of real materials.

Topics for Quantum Mechanics II

Single particle analysis

- **Single particle interacting with electromagnetic fields – EC Chap. 9**
- **Scattering of a particle from a spherical potential – EC Chap. 14**
- **More time independent perturbation methods – EC Chap. 12, 13**
- **Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6**
- **Time dependent perturbation methods – EC Chap. 15**
- **Relativistic effects and the Dirac Equation – EC Chap. 16**
- **Path integral formalism (Feynman) – EC Chap. 11.C**

Multiple particle analysis

- **Quantization of the electromagnetic fields – EC Chap. 17**
- **Photons and atoms – EC Chap. 18**
- **Multi particle systems; Bose and Fermi particles – EC Chap. 10**
- **Multi electron atoms and materials -- various internet sources**
  - **Hartree-Fock approximation & density functional treatment of atoms**
  - **Hartree-Fock approximation & density functional treatment of molecules and solids**

In these first lectures, we will focus on treatment of an atom.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 10	Multielectron atoms		
	Fri: 04/10/2020	No class	*Good Friday*		
29	Mon: 04/13/2020	Chap. 10	Multielectron atoms	#23	04/15/2020
30	Wed: 04/15/2020				
31	Fri: 04/17/2020				
32	Mon: 04/20/2020				
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

The homework problem for this lecture involves evaluating some of the integrals we have been discussiong

Your questions –

From Trevor:

1. On the last line of slide 18, why is the exchange potential multiplied by phi_i?
2. On slide 19, what does alpha represent? Is it related to the indexing alpha that appears on the last slide?

From Surya:

1. Does HF approximation apply for Bosonic Partilces?
2. How is the Lagrange multiplier introduced?

Answers/comments will follow --

Slides from original lecture --

Review and motivation

General considerations in the study of multiple electron systems

- **The wave function for the multiple electron system should take into account the properties of indistinguishable Fermi particles**
- **The particular systems that we would like to model (atoms, molecules, solids…) also generally have both electronic coordinates as well as nuclear coordinates. For the moment, we will neglect the nuclear coordinates and just focus on the electron behaviors**
- **Special tricks have been developed for the treatments of atoms, diatomic molecules, more complicated molecules, and extended systems (solids). In general, simple systems can treated in greater detail/accuracy than can more complicated systems. For example, consider the detailed atomic spectroscopy studied for all of the atoms in the periodic table**

Which of these systems interest you?

Example from the NIST website

NIST Atomic Spectra Database Levels Data

Fe I 847 Levels Found

***Z* = 26, Fe isoelectronic sequence**

Configuration	Term	*J*	Level (eV)
$3d^64s^2$	a ^{5}D	4	0.0000000
		3	0.05156912
		2	0.08728574
		1	0.11011433
		0	0.12126572
$3d^7(^4F)4s$	a ^{5}F	5	0.85899575
		4	0.91460216
		3	0.95815732
		2	0.99011114
		1	1.01105567
$3d^7(^4F)4s$	a ^{3}F	4	1.48486438
		3	1.55735732
		2	1.60789576
$3d^7(^4P)4s$	a ^{5}P	3	2.17594511
		2	2.19786638
		1	2.22271207
$3d^64s^2$	a ^{3}P2	2	2.27860464
		1	2.42419829
		0	2.48437253
$3d^6(^5D)4s4p(^3P°)$	z ^{7}D°	5	*2.39920469*
		4	*2.42543330*
		3	*2.44955976*
		2	*2.46883471*
		1	*2.48211838*
$3d^64s^2$	a ^{3}H	6	2.40407442
		5	2.43269468
		4	2.45343042

Last week, we introduced the NIST Atomic Spectra Database. Here is another example – Fe which shows some of the complexity involved with transition metal materials.

Why is this important?

1. **It is not really ..**
2. **It could be useful for testing experiment/theory**
3. **It could be useful for certain types of measurements**
4. **It may be important for atom lovers, but means nothing to the study of molecules and solids**

Plan –

1. **Discuss the general equations for multielectron systems**
2. **Discuss the Hartree-Fock treatment**
3. **Set up the particular equations for atoms**
4. **How to analyze systems beyond the Hartree-Fock approximation**

Surya's question – does the Hartree-Fock approximation work for multi bose systems?
Quick answer, the general approach can be adopted, but some of the equations need to modified. Examples??

Discussion points

General equations for multi electron systems

We have established that in order to represent N indistinguisable Fermi particles: the wave function must have the property:

$$\psi(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i...\mathbf{r}_j...\mathbf{r}_N) = -\psi(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_j...\mathbf{r}_i...\mathbf{r}_N)$$

For example, we can construct a wave function that has the correct antisymmetry from combinations of single particle states $\varphi_a(\mathbf{r}),\varphi_b(\mathbf{r}),\varphi_c(\mathbf{r})....$

Example for N particles using Slater determinant:

$$\psi(\mathbf{r}_1,\mathbf{r}_2....\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix} = \prod_{i=1}^{N} f_i^\dagger \left|0\right\rangle$$

Review of the properties of identical Fermi particles.

In general, the Hamiltonian of the system takes the form:

$$H(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = \sum_{i=1}^{N} h(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j=1(i \neq j)}^{N} v(\mathbf{r}_i, \mathbf{r}_j)$$

Here $v(\mathbf{r}_i, \mathbf{r}_j) = \dfrac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ representing electron-electron repulsion

For an atom having atomic number Z, $h(\mathbf{r}_i) = -\dfrac{\hbar^2}{2m}\nabla_i^2 - \dfrac{Ze^2}{r_i}$

Identification of one-electron and two-electron terms.

If we choose our single particle basis as eigenstates of the single particle Hamiltonian: $h(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) \equiv \varepsilon_a \varphi_a(\mathbf{r}_1)$

Second quantized version of the multi electron system:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N) \Rightarrow \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here v_{ijkl} denotes matrix elements such as

$$v_{ijkl} = \left\langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \middle| v(\mathbf{r}_1 - \mathbf{r}_2) \middle| \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \right\rangle$$

Second quantization formulation.

For the more general choice of single particle basis $\varphi_a(\mathbf{r})$:

(note the basis functions must be orthonormal: $\langle \varphi_a(\mathbf{r}) | \varphi_b(\mathbf{r}) \rangle = \delta_{ab}$)

Second quantized version of the multi electron system:

$$H(\mathbf{r}_1, \mathbf{r}_2, .. \mathbf{r}_N) \Rightarrow \sum_i h_{ii} f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here h_{ii} denotes single particle matrix elements

$$h_{ii} = \langle \varphi_i(\mathbf{r}) | h(\mathbf{r}) | \varphi_i(\mathbf{r}) \rangle$$

Here v_{ijkl} denotes two particle matrix elements

$$v_{ijkl} = \langle \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) \rangle$$

In this case, the basis functions are not necessarily eigenfunctions of the single particle Hamiltonian.

How can we estimate the ground state of our multi electron Hamiltonian?

variational approach --

Consider a Hamiltonian H having lowest eigenvalue E_0 :

It can be shown that for any function ψ

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

Proof: The Hamiltonian has a complete set of eigenvalues and eigenvectors: $H|\varphi_i\rangle = E_i|\varphi_i\rangle$

Expanding $|\psi\rangle$ in eigenvector basis: $|\psi\rangle = \sum_i C_i|\varphi_i\rangle$

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_i |C_i|^2 E_i}{\sum_i |C_i|^2} \geq E_0$$

Review of the variational principle.

Significance of this inequality --

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

The inequality motivates a class of estimation methods known as variational methods to converge to the ground state energy E_0 and the corresponding ground state probability amplitude.

Define $E_{trial}(\Psi_{trial}) \equiv \dfrac{\langle \psi_{trial} | H | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle}$

Minimize $E_{trial}(\Psi_{trial})$ with respect to Ψ_{trial}

The variational principle guarantees that

$E_{trial}(\Psi_{trial}) \geq E_0$

$\Rightarrow$ The better the trial wavefunction, the better the estimate.

Review continued.

Hartree-Fock approximation

Reverence to the historical paper by Hartree and Hartree

Self-Consistent Field, with Exchange, for Beryllium

By D. R. HARTREE, F.R.S., and W. HARTREE

(*Received February* 25, 1935)

1—INTRODUCTION

Except for the lightest atoms, most calculations of approximate wave functions and fields for many-electron atoms have been carried out by the method of the "self-consistent field," of which the principle is, shortly, the determination of a set of one-electron wave functions such that each represents a stationary state of an electron in the field of the nucleus and the Schrödinger charge distribution of the electrons occupying the other wave functions of the set.† This method has been found quite practicable for numerical work, even for the heaviest atoms.

The Hartree-Fock approximation is based on the choice of

$\left|\Psi_{trial}\right\rangle = \prod_{i=1}^{N} f_i^\dagger \left|0\right\rangle$ using the second quantized notation or

the equivalent Slater determinant based on the single particle functions $\varphi_i(\mathbf{r})$ with the constraint $\left\langle \varphi_i(\mathbf{r}) \middle| \varphi_j(\mathbf{r}) \right\rangle = \delta_{ij}$

$$E_{trial} = \sum_{i=1}^{N} h_{ii} + \frac{1}{2}\sum_{i,j=1}^{N} \left(v_{ijij} - v_{ijji} \right)$$

Note that the *i=j* contribution cancels out.

Second quantization formulation

Matrix elements

$$h_{ii} = \int d^3r \; h(\mathbf{r}) \left|\varphi_i(\mathbf{r})\right|^2$$

$$v_{ijij} = e^2 \int d^3r \int d^3r' \frac{\left|\varphi_i(\mathbf{r})\right|^2 \left|\varphi_j(\mathbf{r}')\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|}$$

$$v_{ijji} = e^2 \delta_{\sigma_i \sigma_j} \int d^3r \int d^3r' \frac{\left(\varphi_i(\mathbf{r})\varphi^*{}_j(\mathbf{r})\right)\left(\varphi^*{}_i(\mathbf{r}')\varphi_j(\mathbf{r}')\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}$$

Constrained optimization

$$\delta\left(E_{trial}\left(\{\varphi_i\}\right) - \sum_{i,j=1}^{N} \lambda_{ij} \left\langle \varphi_i \middle| \varphi_j \right\rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

Writing out the integrals.

Constrained optimization

$$\delta\left(E_{trial}\left(\{\varphi_i\}\right) - \sum_{i,j=1}^{N} \lambda_{ij} \left\langle \varphi_i \middle| \varphi_j \right\rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

Lagrange multiplier

Equations to solve:

$$\frac{\delta E_{trial}}{\delta \varphi_i^*} = H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r})$$

$$H_{eff}(\mathbf{r}) = h(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{Exchange}(\mathbf{r})$$

When these equations are used to find the ground state, we note that

$$\sum_{i=1}^{N} \left|\varphi_i(\mathbf{r})\right|^2 = n(\mathbf{r})$$ electron density

Equations resulting from orbital optimization.

Digression on Lagrange multipliers

$$\delta\left(E_{trial}\left(\{\varphi_i\}\right) - \sum_{i,j=1}^{N} \lambda_{ij} \left\langle \varphi_i \middle| \varphi_j \right\rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

Note that the Lagrange multipliers allow us to solve several equations at once. $\delta E_{trial}\left(\{\varphi_i\}\right)$ and $\delta \left\langle \varphi_i \middle| \varphi_j \right\rangle = 0$

The values of λ_{ij} are determined by requiring the extra conditions $\left\langle \varphi_i \middle| \varphi_j \right\rangle = \delta_{ij}$

Hartree-Fock equations to solve

$$H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r})$$

$$H_{eff}(\mathbf{r}) = h(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{Exchange}(\mathbf{r})$$

$$V_{Hartree}(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

In Hartree-Fock theory, the Fock contribution is actually an integral form:

$$V_{Exchange}(\mathbf{r})\varphi_i(\mathbf{r}) = -e^2 \sum_{j=1}^{N} \delta_{\sigma_i\sigma_j} \int d^3r' \frac{\left(\varphi_i(\mathbf{r}')\varphi^*{}_j(\mathbf{r}')\right)}{|\mathbf{r} - \mathbf{r}'|} \varphi_j(\mathbf{r})$$

Shorthand notation not truly a multiplication

Simplified structure of equations.

Self-consistent solution of the Hartree-Fock equations

Guess one electron functions $\{\varphi_i(\mathbf{r})\}^0$

Count=0

Solve differential integral equations

$H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r}) \quad \Rightarrow \{\varphi_i(\mathbf{r})\}^{new}$

Count=Count+1

$\{\varphi_i(\mathbf{r})\}^{\text{Count}} = \alpha\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} + (1-\alpha)\{\varphi_i(\mathbf{r})\}^{new}$

test: if $\left|\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} - \{\varphi_i(\mathbf{r})\}^{\text{Count}}\right| > \epsilon$

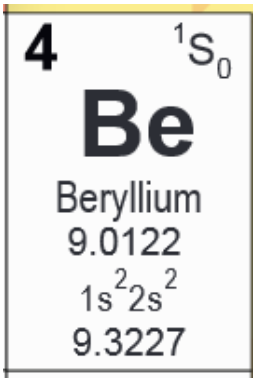
Continue self-consistent Iterations; here α is a calculational parameter

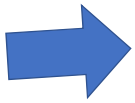
if $\left|\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} - \{\varphi_i(\mathbf{r})\}^{\text{Count}}\right| < \epsilon$

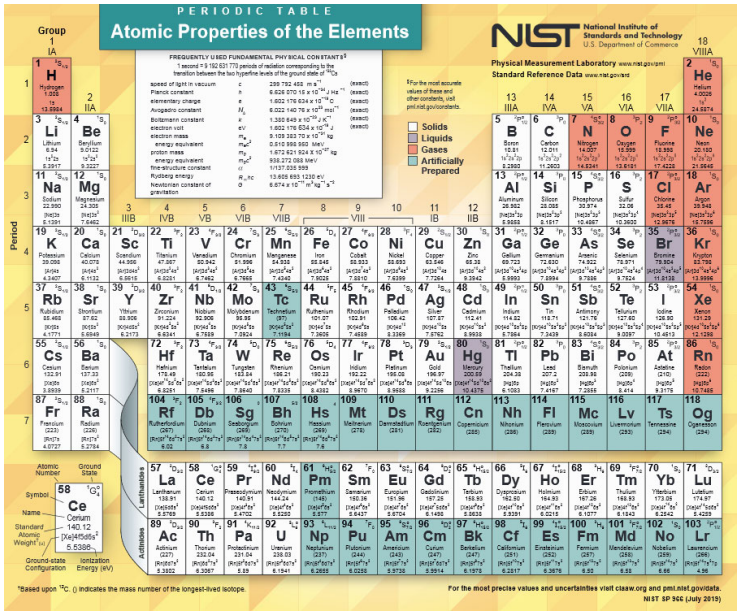
Self-consistent cycles converged

Iteration process in order to achieve self-consistency.

https://www.nist.gov/system/files/documents/2019/12/10/nist_periodictable_july2019_crop.pdf







Details discussed in paper by Hartree and Hartree.

Example studied by Hartree and Hartree.

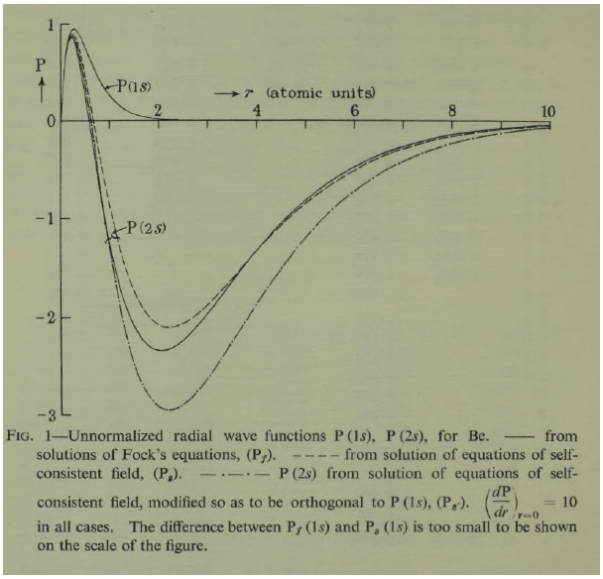


FIG. 1—Unnormalized radial wave functions P(1s), P(2s), for Be. —— from solutions of Fock's equations, (P_f). – – – – from solution of equations of self-consistent field, (P_s). — · — · — P(2s) from solution of equations of self-consistent field, modified so as to be orthogonal to P(1s), ($P_{s'}$). $\left(\frac{dP}{dr}\right)_{r=0} = 10$ in all cases. The difference between P_f(1s) and P_s(1s) is too small to be shown on the scale of the figure.

Plot of radial wave functions from paper.

Other methods of solving the Hartree Fock equations

Rather than solve the coupled integral-differential radial equations, it is popular in quantum chemical contexts to represent the single particle functions as a sum of particular (fixed) basis functions. The variational parameters are then the linear coefficients of the basis functions

$$\varphi_i(\mathbf{r}) = \sum_\alpha C_\alpha^i \chi_\alpha(\mathbf{r})$$

Alternative method for carrying out Hartre-Fock analysis.